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Orientation Determination of Zinc Crystals by the Light-Figure Method*

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Synopsis

The application of the light-figure method to the determination of orientations of zinc single crystals was studied thoroughly. This technique of orientation determination may be conducted with the simple apparatus and procedure and with high precision within ± 0.1°, of which full accounts are given with reference to various examples of actual orientation determinations.

I. Introduction

When a fine pencil of light is allowed to fall on the surface of a crystal, etched beforehand with a proper reagent, light reflected by an etched crystal plane forms on a screen a light-pattern of the same symmetry as that of the reflected plane. This so called light figure is made by the reflection of light by facets of etch figures produced by etching on the surface of the crystal. So, the form of of etch figures and consequently that of light figures changes diversely with etching conditions (the etching reagent, its temperature and the time of etching). Whatever the form of light figures may be, however, their symmetry characteristics naturally remain the same. Namely, in cubic crystals light figures of the tetragonal, digonal and trigonal symmetry are produced inevitably by the {100}, {110} and {111} planes, respectively, and in hexagonal crystals light figures of the hexagonal and digonal symmetry are created by the {0001} and $\{11\bar{2}0\}$ or $\{10\bar{1}0\}$ planes, respectively(see Fig. 1～9 shown later). Then, when the center of symmetry of a light figure is made to coincide with a pinhole of a screen set perpendicular to incident light, the incident light becomes perpendicular to the reflecting crystal plane, that is, the travelling direction of light coincides with the <100>, <110> or <111> axis corresponding, respectively, to the light figure of the {100}, {110} or {111} plane in cubic crystals or with the <0001>, $<11\bar{2}0>$ or $<10\bar{1}0>$ axis corresponding, respectively, to the light figure of the {0001}, $\{11\bar{2}0\}$ or $\{10\bar{1}0\}$ plane in hexagonal crystals. Accordingly, the crystal orientation may be determined by measuring

* The 567th report of the Research Institute for Iron, Steel and Other Metals. The original of this report written in Japanese was published previously in Nippon Kinzoku Gakkai-shi (J. Japan Inst. Metals), 13 (1949), No. 4.

angles between those principal crystallographic directions and the geometrical axis of a specimen crystal.

This method of utilizing light figures for determining crystal orientations has the following advantages: (1) The apparatus required is simple and relatively cheap, (2) a crystal specimen can readily be mounted on the apparatus after a short-time etching with a suitable reagent, even if its size is fairly large, (3) the determination can be made simply and accurately, and (4) it has a possibility of being applicable to single crystals of any metal. It only need know beforehand propor directions of etching and corresponding light figures. In this connection, it is to be noted that necessary conditions for etching required for determining crystal orientations rapidly and accurately by the light-figure method are as follows: (1) Distinct light figures having a definite center of symmetry should be obtained, (2) the time of etching for producing suitable light figures must possibly be short, and (3) though a slight and uniform reduction of the volume of a specimen crystal can not naturally be avoidable, its form must not vary appercia-bly and moreover its surface must not become rough.

The senior of the present writers(1) previously reported on the determination of orientations of cubic metal crystals by the use of light figures, and since he has constantly applied this method to single crystals of nickel, copper, iron, aluminium, face-centered nickel-iron alloys, and iron-silicon alloys with great success(2). The present writers recently have obtained very satisfactory results in the application of light-figure method to the determination of orientations of zinc crystals. We give in this report a detailed description of the actual application of the light-figure method to the orientation determination of hexagonal crystals like zinc, as the procedure for hexagonal crystals differs in many respects from that for cubic ones.

It is to be remarked that we have recently found Jakowlewa's(3) paper on the determination of orientations of zinc and cadmium crystals by the use of light figures. By the procedure different from ours, he determined only the angle which the rod axis of a specimen crystal makes with the hexagonal axis with an accuracy of $2\sim3^\circ$. Our procedure allows to determine orientations of zinc crystals *perfectly* with an accuracy within $\pm0.1^\circ$, as will be shown later.

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(1) M. Yamamoto ; Nippon Kinzoku Gakkai-shi (J. Japan Inst. Metals), 5 (1941), 214 (in Japanese); Sci. Rep. Tôhoku Imp. Univ., 31 (1943), 121.

(2) As for light figures of cubic metal crystals see: M. Yamamoto, Nippon Kinzoku Gakkai-shi, 4 (1940), 368 (in Japanese); Sci. Rep. Tôhoku Imp. Univ., 29 (1941), 113 (nickel and copper crystals); Nippon Kinzoku Gakkai-shi, 5 (1941), 324 (in Japanese) (iron and aluminium crystals); ibid., 6 (1942), 535 (in Japanese) (nickel crystals); Kagaku (Science), 14 (1944), 67 (in Japanese) (face-centered nickel-iron alloy crystals); M. Yamamoto and J. Watanabé, Not yet published (iron and iron-silicon alloy crystals).

(3) E. Jakowlewa, Phys. Z. Sowjetunion, 3 (1933), 429.

II. Apparatus, geometrical relations, etching technique and procedures for the determination of crystal orientations

A. Apparatus.

The apparatus, constantly used in our laboratory for determining crystal orientations by the light-figure method, consists of a light source, a system of lens and slits by which white light emitted from the source is concentrated to the surface of a specimen crystal, a white screen with a pinhole by which incident light is made to a pencil and on which a light figure is thrown, and a two-circle goniometer which serves to hold the specimen crystal and to determine orientations, all set in the above-mentioned order on an optical bench in a dark room. The detail of this arrangment was described previously(1).

B. Geometrical relations.

As the principal crystallographic axes of hexagonal crystal, the hexagonal axis [0001] and the digonal axes of the first kind [$2\bar{1}\bar{1}0$], [$\bar{1}2\bar{1}0$]. [$\bar{1}\bar{1}20$], four axes in all, are usually taken. If the geometrical axis of a specimen crystal (the rod axis of a crystal rod, normal of a crystal disk, etc.) $\overrightarrow{OP}$ makes an angle θ with an [0001] axis and angles α, β and γ with [$2\bar{1}\bar{1}0$], [$\bar{1}2\bar{1}0$] and [$\bar{1}\bar{1}20$] axes, respectively, the following relationships hold among these angles:

$$\cos\alpha + \cos\beta + \cos\gamma = 0, \tag{1}$$

$$\cos^2\theta = 1-(2/3)(\cos^2\alpha + \cos^2\beta + \cos^2\gamma), \tag{2}$$

or

$$\cos^2\theta = 1-(4/3)(\cos^2\alpha + \cos\alpha\cdot\cos\beta + \cos^2\beta), \tag{3}$$

and

$$\cos\beta \text{ or } \cos\gamma = (1/2)[-\cos\alpha \pm \sqrt{3(1-\cos^2\theta-\cos^2\alpha)}]. \tag{3a}$$

Accordingly, the orientation of $\overrightarrow{OP}$ can be fixed by specifying any two of θ, α, β and γ. Besides, there exist the same relations as above-mentioned among angles α', β' and γ' which $\overrightarrow{OP}$ makes with the digonal axes of the second kind [$10\bar{1}0$], [$\bar{1}100$] and [$0\bar{1}10$], respectively, and the angle θ, namely,

$$\cos\alpha' + \cos\beta' + \cos\gamma' = 0, \tag{4}$$

$$\cos^2\theta = 1-(2/3)(\cos^2\alpha' + \cos^2\beta' + \cos^2\gamma'), \tag{5}$$

or

$$\cos^2\theta = 1-(4/3)(\cos^2\alpha' + \cos\alpha'\cdot\cos\beta' + \cos^2\beta'), \tag{6}$$

and

$$\cos\beta' \text{ or } \cos\gamma' = (1/2)[-\cos\alpha' \pm \sqrt{3(1-\cos^2\theta-\cos^2\alpha')}], \tag{6a}$$

and further the following relations hold among α', β', γ', α, β and γ:

$$\left.\begin{aligned} \cos\alpha &= (\cos\alpha'-\cos\beta')/\sqrt{3}, \\ \cos\beta &= (\cos\beta'-\cos\gamma')/\sqrt{3}, \\ \text{and}\quad \cos\gamma &= (\cos\gamma'-\cos\alpha')/\sqrt{3}. \end{aligned}\right\} \tag{7}$$

C. Etching technique.

As may be understood from the description in the introduction, the angle θ can be determined directly by the use of light figure produced by the {0001} plane, and angles α, β and γ by light figures on the {$11\bar{2}0$} planes and α', β' and γ' by light figures on the {$10\bar{1}0$} planes. For such determinations, however, it is necessary to use distinct light figures having a definite center of symmetry, as already stated. We had studied on light figures of zinc crystals etched with various reagents, especially with the aim of finding out light figures, suitable to the orientation determination, the results of which was published previously(4). Proper directions of etching and corresponding light figures found by us are summarized

Table 1. Directions for etching zinc crystals for determining their crystal orientations by the light-figure method.
The mark ◎ denotes a distinct figure, suitable to the determination of crystal orientations, ○ a distinct, but not so suitable, figure, △ a distinct, but unsuitable, figure and × an indistinct or no figure.

No.	Etching reagents*	Distinctness and suitablity of light figure on			Optimum etching time	Form of light figure on		
		{0001}	$\{11\bar{2}0\}$	$\{10\bar{1}0\}$		{0001}	$\{11\bar{2}0\}$	$\{10\bar{1}0\}$
1a	100% HCl	◎	○	△	5 sec.	Fig. 1	—	—
1b	50% 〃	◎	○	△	2～3 min.	Fig. 2	—	—
1c	5% 〃	◎	○	△	15～25 min.	〃	—	—
2 a &b	10 and 5% H_2SO_4	◎	○	△	10～15min.	Fig. 3	—	—
3a	100% HF	◎	×	×	5～10 min.	Fig. 4	—	—
3b	50% 〃	◎	×	×	3～5 min.	Fi3. 5	—	—
4	Boiling saturated aqueous solution of NaOH	◎	◎	◎	40 min.	Fig. 6	Fig. 7	Fig. 8
5	Boiling saturated aqueous solution of KOH	◎	◎	◎	20 min.	〃	〃	〃
6a	Mixed solution of both saturated aqueous solutions of Na_2SO_4 and CrO_3 (95 : 5)	◎	×	○	>5～10 min.	Fig. 5	—	—
6b	〃 (92 : 8)	◎	○	○	>1 min.	〃	—	—
6c	〃 (90 : 10)	◎	○	○	>3 min.	〃	—	—
6d	〃 (87 : 13)	◎	○	○	>2 min.	Fig. 9	—	—
6e	〃 (85 : 15)	◎	○	○	>1 min.	〃	—	—
6f	〃 (80 : 20)	◎	○	○	>2 min.	〃	—	—
7 a &b	50 and 5% aqueous solution of $(NH_4)_2S_2O_8$	◎	×	×	10～20 min.	Fig. 5	—	—

* Concentrations of etchants are expressed in relative to that of "concentrated" acid or a saturated solution of alkalis and salts as 100 per cent. If the desired light figure were not observed by etching with this reagent, etch a specimen crystal preliminarily with concentrated nitric acid for several seconds and then apply the specified etching.

in Table 1, which indicates that, for the perfect determination of crystal orientations, that is, for the determination of θ as well as α, β and γ, boiling saturated aqueous solution of sodium hydroxide or of potassium hydroxide is most suitable; the latter solution being more suitable owing to the shortness of the etching time required. Other etchants are suitable only for determining θ, but insufficient or unsuitable for determining α, β and γ because of inadequate forms of produced light figures or the long etching-time required.

D. Procedures.

A specimen crystal, having been properly etched beforehand, is mounted on a

(4) M. Yamamoto and J. Watanabé, Nippon Kinzoku Gakkai-shi, **13** (1949), No. 3; **14B** (1950), No. 2 (Both in Japanese); Sci. Rep. RITU, **2** (1950), 81.

two-circle goniometer with its rod axis perpendicular to the vertical circle of the goniometer, and a light figure produced by a principal crystallographic plane is catched on a screen by rotating the specimen crystal about its rod axis. Then, positions of the two circles of the goniometer are so adjusted that the center of symmetry of the light figure may coincide with a pinhole of the screen, and the

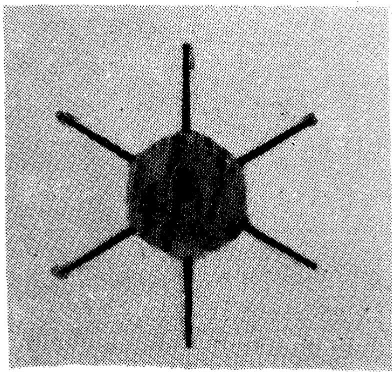

Fig. 1. See Table 1.

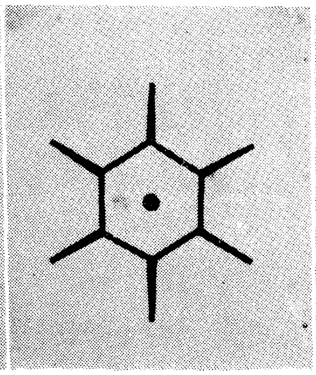

Fig. 2. See Table 1.

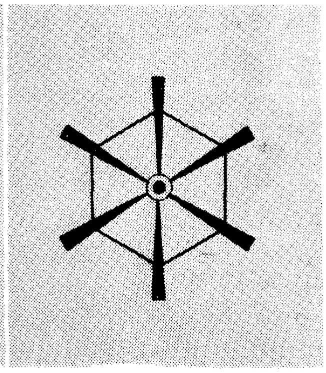

Fig. 3. See Table 1.

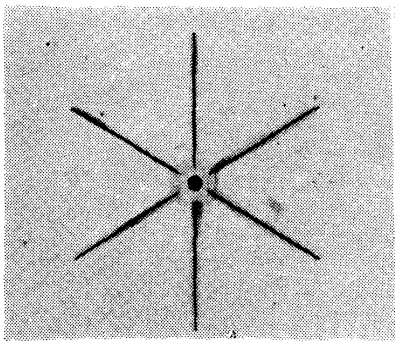

Fig. 4. See Table 1.

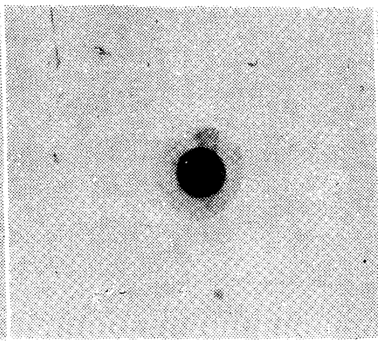

Fig. 5. See Table 1.

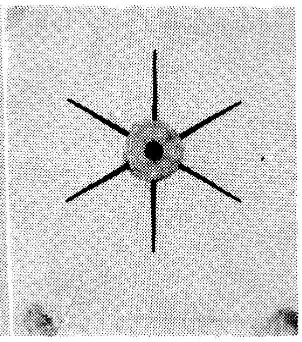

Fig. 6. See Table 1.

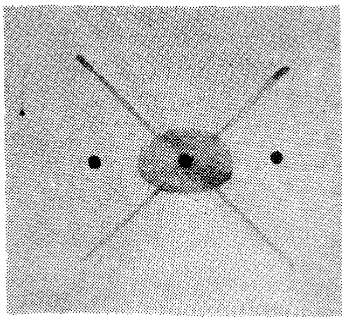

Fig. 7. See Table 1.

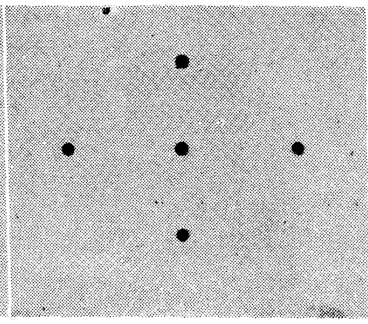

Fig. 8. See Table 1.

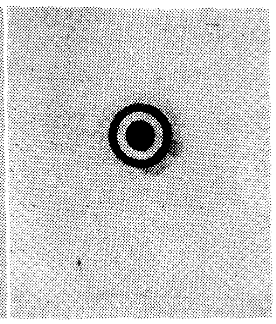

Fig. 9. See Table 1.

reading of angle on the horizontal circle, φ_1, is recorded. After the specimen crystal has been rotated by 180° about its rod axis and then by so much angle about the vertical axis of the goniometer that the same light figure may be catched again on the screen, the reading of angle on the horizontal circle, φ_2, is taken. Then, an angle determined by an equation

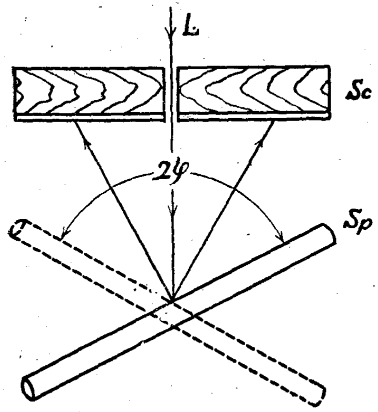

Fig. 10. To illustrate the procedure for determining crystal orientations by the light-figure method.
L: light pencil, Sc: screen with a pinhole, Sp: specimen crystal.

$$\varphi = (\varphi_1 \sim \varphi_2)/2 \quad (8)$$

gives the angle between the rod axis of the specimen crystal and the crystallographic axis concerned (Fig. 10). The same procedure may be repeated with light figures on other crystallographic planes. When any two of the four angles θ, α, β and γ can be determined in such a way, other two unknown angles may be calculated from Eqs. (1), (3), and (3a). Or, when any two of the other set of four angles θ, α', β' and γ can be measured, other two angles may be calculated from Eqs. (4), (6) and (6a) and then α, β and γ may be determined by Eqs. (7).

It should be noted that actual determinations of crystal orientations can be made by the use of light figures when any two of any set of four angles are greater than about 40°, regardless of the size of crystal specimens, as seen from the actual examples shown later. When these angles are less than about 40°, light figures concerned cannot or hardly be observed. Generally, when it is possible to determine directly the angle θ, any two or, one at least, of α, β and γ are measurable, but, in most cases, one of the two measured values would be inaccurate since it is less than about 40°. When θ can not be determined directly, it is possible to measure any two of α, β and γ or all of these three angles in the most favourable case, though one of the three measured values is inaccurate since it is greater than 140°. After all, any two of any set of four angles can always be determined accurately.

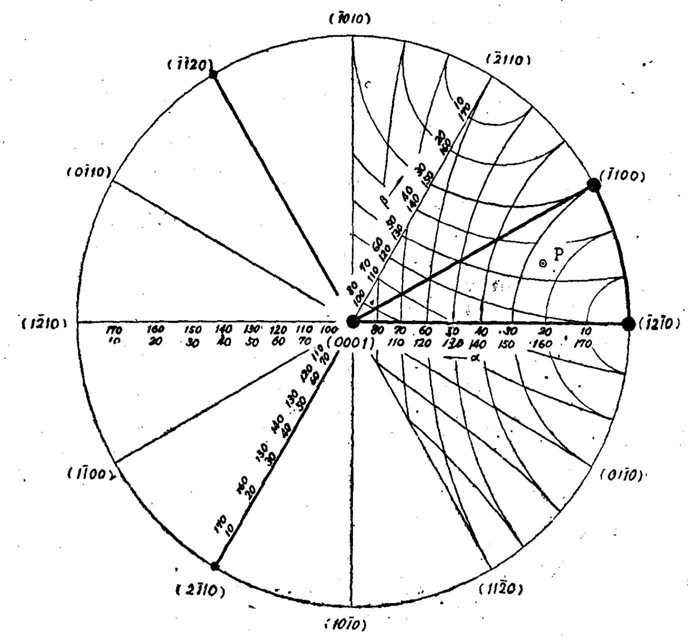

Fig. 11. Standard stereographic projection of hexagonal crystal. Plane of projection: (0001).

E. Stereographic representation of crystal orientations.

It is convenient for the mutual comparison to represent the determined crystal orientations by the stereographic projection.(5) For this purpose, a standard

(5) For the stereographic projection, see, for example, C. S. Barrett, Trans. A.I.M.E., 124 (1937), 29.

projection, which is projected on {0001} plane, is used in general and on it a crystal orientation is plotted as a point like P in Fig. 11*, which is apart from the principal crystallographic axes by given angular distances. It is to be noted, however, that it is not always necessary to employ the whole of the standard projection, because angles between a crystal orientation and the three neighbouring poles of {0001}, {11$\bar{2}$0} and {10$\bar{1}$0} planes are the same in any of twelve stereographic triangles of the standard projection which are made by drawing great circles through the poles of principal crystal planes. Accordingly, one of these triangles, such as shown by heavy lines in Fig. 11, is used for plotting crystal orientations, and any two of angles α, β and γ between the rod axis of a specimen crystal and <11$\bar{2}$0> axes are plotted on the triangle with aids of the Wulff net. The point P shown in Fig. 11 represents the orientation $\alpha = 25^\circ$ and $\beta = 135^\circ$. It is to noted that the inclination of the rod axis to the hexagoanl axis <0001>, namely θ, cannot directly be determined from the above plotting, and it can be read by the use of a polar net or calculated by means of Eq. (3).

III. Actual examples and accuracy of orientation determinations

Now, we present various typical examples of actual determination of orientations of zinc crystals with the light-figure method. Crystal specimens used were produced by us with the Tammann-Bridgman method of the lowering-crucible type. They are of a cylindrical form, having a sharp end from which the crystallisation started; their dimensions are $4 \sim 14$ mm in diameter and $1 \sim 15$ cm in length excluding a tapered part. These crystals, etched beforehand with concentrated nitric acid for several seconds, were again etched with boiling saturated aqueous solution of potassium hydroxide for about 20 minutes (Table 1, No. 5) and then set on the goniometer. The angles between the rod axis and the principal crystallographic axes were measured at several positions (one position for short crystals and three positions for long ones) of an uniform part of a crystal rod. The measurement of angles was made thrice at each position and the mean value was taken as the final one. Two actual examples of the measurement of the angles are shown in Table 2, from which the accuracy of the determination may be estimated as within $\pm 0.1^\circ$.

Table 3 shows various examples of crystal orientations as determined by the light-figure method. For crystals No. 16, 294 and 504, two angles, θ and α, could be measured accurately and other two angles, β and γ, were calculated by Eq. (3a). For crystals No. 152 and 377, α and β were measured, and θ and γ were computed by Eqs. (3) and (1), respectively.

For crystal No. 59, three angles, α, β and γ, were measured. Though $\sum = \cos\alpha + \cos\beta + \cos\gamma$ should be equal to zero by Eq. (1), the value of $\sum$ calculated from the measured data for α, β and γ is 0.005. This practically zero value, however, indicates that any of the three measured data may be very accurate. In fact, the

* In Fig 11, (2$\bar{1}$10) is really (2$\bar{1}\bar{1}$0).

Table 2. Two actual examples of the determination of crystal orientations of zinc single crystals by the light-figure method.

(a) Crystal No. 377 (Diameter 3.5 mm; Length 9.0 cm)

Measured point, No.	α (in degree)			β (in degree)		
	Measured value	Mean value at each point	Final mean	Measured value	Mean value at each point	Final mean
1	78.7 .8 .8	78.8	78.7	82.5 .6 .4	82.5	82.6
2	78.9 .8 .7	78.8		82.6 .5 .6	82.6	
3	78.4 .6 .8	78.6		82 7 .4 .8	82.6	

(b) Crystal No. 504 (Diameter 3.8 mm; Length 5.0 cm)

Measured point, No.	θ (in degree)			α (in degree)		
	Measured value	Mean value at each point	Final mean	Measured value	Mean value at each point	Final mean
1	81.5 .6 .8	81.6	81.5	101.6 .5 .5	101.6	101.5
2	81.4 .5 .4	81.4		101.6 .6 .4	101 5	
3	81.6 .5 .6	81.6		101.6 .4 .4	101.5	

values for θ calculated from Eq. (3) by the use of the three pairs of the measured values for α, β and γ are 26.7°, 26.5° and 26.4°, and the value for θ calculated from Eq. (2) by the use of all the three measured values is 26.5°, all coinciding with each other within the range of experimental error. It is to be noted that all of the three angles, α, β and γ, can seldom be measured with such a great accuracy.

For crystal No. 493, all of the four angles, θ, α, β and γ, were measured. But, the computed value of $\sum$ is -0.048, deviating so appreciably from zero that the determination of all or some angles may be inaccurate. In fact, the value for θ computed from Eq. (2) by the use of measured data for α, β and γ is 42.8°, while the measured value of θ, which is always considerably accurate, is 43.8°, the difference being 1.0°. On the other hand, values for θ calculated from Eq. (3) by the use of measured data for α and β, β and γ, and γ and α, is 40.4°, 44.6° and 43.6°, respectively, the last calculated data coinciding well with the measured one. Thus, it may be seen that the most inaccurate is the measured data for β, which is 81.7°. Further, the value for β computed from Eq. (1) by the use of measured data for α and γ is 79.0°, and values for β and γ computed from the

Table 3. Various examples of crystal orientations of zinc single crystals, as determined by the light-figure method.

(M) and (C) mark, respectively, the measured and the computed values, and $\sum$ in Remarks denotes $\cos\alpha+\cos\beta+\cos\gamma$, which should be zero.

Crystal o.	Diameter mm	Length cm	No. of measured points	θ degree	α degree	β degree	γ degree	Remarks
16	13.3	0.8	1	80.2 (M)	88.4 (M)	33.0 (C)	150.1 (C)	
59	13.6	1.5	2	26.5 (C) 26.7 (C) 26.5 (C) 26.4 (C)	83.4 (M) 83.4 (M) 83.7 (C) 83.4 (M)	71.4 (M) 71.4 (M) 71.4 (M) 71.7 (C)	115.9 (M) 115.7 (C) 115.9 (M) 115.9 (M)	$\sum=+0.005$ Equally accurate
152	8.4	1.3	2	1.5 (C)	91.0 (M)	90.3 (M)	88.7 (C)	
294	4.7	3.2	3	67.0 (M)	78.7 (M)	47.1 (C)	151.2 (C)	
377	3.5	9.0	3	19.1 (C)	78.7 (M)	82.6 (M)	109.0 (C)	In Table 2.
493	4.0	9.0	3	43.8 (M) 43.8 (M) 43.8 (M) 43.8 (M) 42.8 (C) 40.4 (C) 44.6 (C) 43.6 (C)	61.6 (M) 61.6 (M) 59.1 (C) 60.4 (C) 61.6 (M) 61.6 (M) 58.5 (C) 61.6 (M)	81.7 (M) 78.6 (C) 81.7 (M) 80.1 (C) 81.7 (M) 81.7 (M) 81.7 (M) 79.0 (C)	131.8 (M) 132.4 (C) 131.2 (C) 131.8 (M) 131.8 (M) 138.3 (C) 131.8 (M) 131.8 (M)	$\sum=-0.048$ Most accurate More accurate Most accurate
497	4.0	5.1	3	84.7 (M) 84.7 (M) 84.7 (M) 76.6 (C)	60.9 (M) 60.9 (M) 59.4 (C) 60.9 (M)	60.9 (M) 59.4 (C) 60.9 (M) 60.9 (M)	...... 174.3 (C) 174.3 (C) 166.6 (C)	Inaccurate Accurate Inaccurate
504	3.8	5.0	3	81.5 (M)	101.5 (M)	20.0 (C)	137.7 (C)	In Table 2
517	3.6	6.0	3	64.5 (M)	25.0 (C)	117.5 (C)	116.2 (C)	$\alpha' = 89.3°$
530	4.1	4.0	3	89.9 (M) 89.9 (M) 89.9 (M) 86.9 (C)	67.8 (M) 67.8 (M) 67.7 (C) 67.8 (M)	52.3 (M) 52.2 (C) 52.3 (M) 52.3 (M)	...... 172.2 (C) 172.3 (C) 171.7 (C)	 Inaccurate

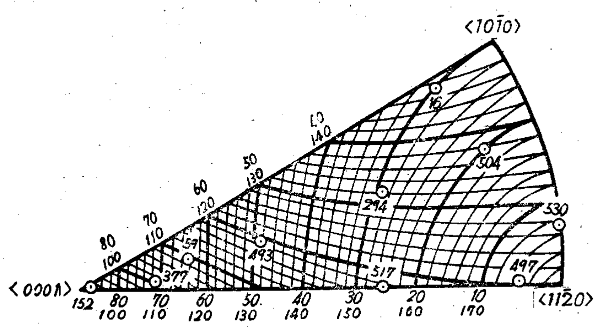

Fig. 12. Stereographic representation of orientations of zinc crystals, as determined by the light-figure method.

measured data for θ and α are 78.6° and 132.4°, respectively. These computed values for β agree well with each other, and the computed value for γ coincides well with the measured one (131.8°). Values for α and β computed by the use of measured data for θ and γ are 60.4° and 80.1°, respectively. These values differ appreciably from the measured value for α (61.6°) and the correct computed value for β (79.0°), respectively. Thus, it may be concluded that the measured data for α is the most accurate and the measured one for γ is moderately accurate.

For crystals No. 497 and 530, θ and two of α, β and γ, three angles in all, were determined directly. For No. 497, the calculated value of θ (76.6°) deviates considerably from the measured one (84.7°). Accordingly, it may be supposed that any one of α and β is considerably inaccurate. On the other hand, in the case of No. 530, the computed value of θ (86.9°) also deviates considerably from the measured one (89.9°), but both the calculated values of α and β are in good agreement with the measured ones, and the two computed values for γ agree with each other. Thus, it may be concluded that direct determinations were made with great accuracy and that the deviation of the calculated value of θ from its measured one is due to the abrupt variation of cosine for angles nearly 90° in the neighbourhood of zero.

Finally, for crystal No. 517, θ and α' were measured and β' and γ' were computed from Eq. (6a) by the use of the measured values. Then, α, β and γ were determined by the computation with Eqs. (7). Such cases occur when orientations are near to $<1\bar{1}20>$ axes

Stereographic representation of crystal orientations of zinc crystals, which were given in Table 3, are as shown in Fig. 12.

Summary.

The application of the light-figure method to the determination of orientations of hexagonal zinc single crystals of the cylindrical rod form was investigated thoroughly. The perfect determination of crystal orientations, namely the determination of the four angles which the rod axis of a specimen crystal makes with the hexagonal axis [0001] and the digonal axes of the first kind $[2\bar{1}\bar{1}0]$, $[\bar{1}2\bar{1}0]$ and $[\bar{1}\bar{1}20]$, can be done with the simple apparatus and procedure and with high precision within ±0.1°, of which full accounts are given with reference to various actual examples of orientation determination.

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